Amendment

Please add the following claims:

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13 A method of in-situ soil remediation with a chemical oxidizing agent to reduce the concentration level of a volatile organic contaminant to a target concentration level, comprising the sequential steps of:

a) treating the contaminated soil in-situ by a thermal - stripping process in which the soil is churned by a soil mixing device and hot air is injected into the soil as it is being churned to thermally strip off organic compounds, including the volatile organic contaminant, and

b) determining the concentration level of the volatile organic contaminant remaining after the thermal stripping process

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c) introducing a chemical oxidizing agent into the soil in an amount that is effective over reasonable time to reduce the concentration level to or below the target level.

14. A method as in claim 13, wherein the step of treating the contaminated soil in-situ by a thermal - stripping process is continued until such thermal stripping is no longer practically effective in further reducing the contaminant level of the volatile organic contaminant.

15. A method as in claim 13, wherein the volatile organic contaminant is from the group of:

benzene, ethyl benzene, toluene, xylene, methylene chloride, 1,2-dichloroethane, 1,1,1-trichloroethane (TCA), carbon tetrachloride, chloroform, chlorobenzenes, ethylene dibromide, tertiary butyl ether, tetrachloroethylene (PCE), trichloroethene (TCE), dichloroethene (DCE) and vinyl chloride.

16. A method as in claim 15, wherein the chemical oxidizing agent is permanganate.

Response to Office Action

The claims pending at the time of the November 5, 2002 Office Action were 3-8 and 10-12. This amendment adds claims 13-16.

All claims pending before this amendment were rejected as being obvious under 35 USC 103 (a). Claims 3-5 were rejected as being obvious over US 4,834,194 ("Manchak Jr. '194") in view of US 4,844,807 ("Manchak Jr. '807"). Claim 6 is a dependant claim that was rejected over the same combination and US 5,190405 ("Vinegar et al"). Claims 7-8 and 10-11 were rejected as being obvious over Manchak Jr. '194 in view of Manchak Jr. '807 and US 5,830,752 ("Bruso"). Claim 12 is a dependant claim that was rejected over the same combination and Vinegar et al.

Thus, the primary combination applied by the examiner is Manchak Jr. '194 in view of Manchak Jr. '807 and /or Bruso. The Examiner states that Manchak '194 teaches a method of soil remediation comprising churning or comminuting the soil with a soil mixing device, injecting hot air into the soil as it is churned to strip off the target organic compound, and then introducing a chemical agent such as potassium permanganate into the soil to continue reducing the target contaminant level. [Detailed Action, page 2]. Manchak '194 does not teach such a method. The Examiner also states that claims 15 and 16 of Manchak Jr. '194 disclose that chemical oxidants, such as permanganate, are injected into the soil to neutralize unremoved contaminants, and thus inherently teaches that a chemical treatment is done if needed after the air stripping, and that the difference in cost of permanganate versus air, and the possibly undesirable effects of large amounts of permanganate, would be an implied teaching that air stripping should be used until it is no longer practically effective, and then the permanganate would be used to complete the remediation . [Detailed Action, page 3.]. Applicant believes that the Examiner has

misconstrued the teachings of both Manchak references, and read too much into claims 15 and 16 of Manchak Jr. '194, as described below.

The Examiner appears to rely almost entirely upon the upon the claims 7—16 of Manchak Jr. '194 as somehow contradicting, improving or supplementing the teachings of Manchak Jr. '807 and the specification of Manchak Jr. '194, but those claims do not. Claims 7-13 recite steps used to collect and analyze the contaminants in the soil. Claim 14 then adds the step of treating contaminants that can be removed as vapors or gasses. Claims 15 and 16 add the step of adding a chemical oxidant, such as potassium permanganate, to neutralize unremoved contaminants. To read these steps in conjunction with the specification and with Manchak Jr. '807, as described below, one of skill in the art would see the belief by Manchak that any contaminants that have a boiling point above the temperature of the thermal fluid must be treated by an oxidant. There is no suggestion that a target contaminant that is susceptible to thermal stripping might require oxidation treatment as a final stage, or that the thermal stripping should be used to reduce total oxidant demand before introducing an oxidant.

In fact, the terms permanganate and oxidant do not appear anywhere in Manchak Jr. '194 except in claims 15 and 16. Thus, if Manchack Jr. '194 is considered to have support for such claims, the support must come by its reference to Manchak Jr. '807. Manchack Jr. '194 purports to be an improvement to Manchak Jr. '807 (see excerpts from column 1, below.)

> My co-pending U.S. applications Ser. No. 865,745, filed Aug. 26, 1985 now U.S. Pat. No. 4,776,409, for In Situ Waste Impoundment Treating Apparatus and Method of Using Same and Ser. No. 049,861 **[Manchak Jr. '807]** each disclose apparatus which physically agitates a subsurface volume of soil in situ, and preferably injects a heated fluid such as steam into the agitating soil which then releases volatile components which percolate upwardly through the soil to the ground surface where they can be analyzed. Treatment methods and chemicals are then selected

depending on the composition of the volatile components liberated from the sub-surface soil. [lines 7-19]

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Although the inventions disclosed in my prior pending applications mentioned above perform perfectly well for their intended purposes, the apparatus shown in Ser. Nos. 865,745 and 049,861 **[Manchak Jr. '807]** is designed not only for the purpose of analyzing the composition of soil contaminants but also for treating the soil, if necessary. In general, this results in apparatus which is larger and slower than need be for preliminary site testing where it is desirable to provide analytical results in real time. [lines 32-41]

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Accordingly, it is an object of the present invention to provide an improved method and apparatus for liberating volatile gases from sub-surface soil locations which more quickly conducts the volatiles to the surface to enable analysis of such gases to determine the soil contents in real time. An additional object of the invention is to provide improved treatment methods and apparatus designed to ensure that no contamination of adjacent soil blocks takes place during treatment of the currently treated block or blocks. [lines 48-57]

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SUMMARY OF THE INVENTION

The present invention accordingly provides a method of analyzing soil to determine contaminants therein wherein a block or cylinder of soil is agitated and heated to release volatile contaminants which are then conducted through a relatively unobstructed flow path created in the soil to the surface where they may be analyzed. Two different embodiments of apparatus for performing the method are disclosed. [lines 59-67]

In summary, Manchak Jr. '194 starts with the premise that the apparatus of Manchak Jr. '807 is larger than needed for preliminary site testing, and thus slower in providing a site map of the contaminants at various depths and locations. Manchak Jr. '194 then purports to improve that situation with a smaller apparatus having an annulus cutter on the drill stem to provide a

"relatively unobstructed flow path" to the surface, where the thermally-stripped vapors are analyzed for contaminants.

What Manchak Jr. '194 does not do, however, is contradict or improve any teaching of Manchak Jr. '807 regarding the manner of using chemical oxidizing agents, such as potassium permanganate or sodium permanganate, to treat toxic hydrocarbons. A person skilled in soil remediation would find no indication in Manchak Jr. '194 to suggest that there is anything inefficient or impractical about the teaching of Manchak Jr. '807 regarding the manner of using permanganates to treat toxic hydrocarbons. The same person reading the disclosure of the Applicant's pending application, however, would understand by comparison why the teaching of Manchak Jr.'807 is an inefficient and impractical way to apply permanganates to treat toxic hydrocarbons.

Consider what Manchak Jr. '807 actually teaches regarding the manner of using chemical oxidizing agents, such as potassium permanganate or sodium permanganate, to treat toxic hydrocarbons.

> If the sensing unit indicates that disagreeable odor producing compounds such as certain organics, hydrogen sulphide, sulphur dioxide; water soluble salts of toxic metals; or toxic organic compounds not volatile at the temperature of the steam being used are present, a liquid oxidizing agent such as hydrogen peroxide or an aqueous solution of potassium permanganate is discharged into the zone through the first nozzles when steam is not discharging therefrom.
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> The oxidizing agent transforms the hydrogen sulphide and sulphur dioxide to elemental sulphur, hydrogen and oxygen, and reacts with the major portions of the water-soluble salts of toxic metals to form substantially water insoluble compounds. The oxidizing agent for reasons not understood tends to transform long chain hydrocarbons not volatile at the temperature of the steam being used into shorter chain hydrocarbons that are volatile at the

> steam temperature and flow upwardly into the confined space as toxic vapors. [col.3, lines 37-55]
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> When sensing unit F indicates that toxic hydrocarbons are present in zone A that are not volatile at the temperature of the steam being used, pump G is actuated, and valve 225b opened. Reservoirs 219 contain different liquid reagents that are useful in treating different toxic components that are identified by the sensing unit F. For instance, an aqueous solution of an oxidant such as potassium permanganate may be discharged through nozzles 205 into zone A. For reasons not understood, the potassium permanganate tends to react with long chain hydrocarbons present in zone A to transform them into shorter chain hydrocarbons that are volatile at the temperature of the steam being used and that flow upwardly into confined space 251 as toxic vapors. [col. 9, lines 4 –18]
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> Sampling of the identity and quantity of toxic components in zone A and in the toxic stream is carried out by a sensing unit F. When sensing unit F indicates the presence of toxic hydrocarbons in zone A that are not volatile at the temperature of the steam being used, or disagreeable odor producing compounds such as hydrogen sulphide, sulphur dioxide, mercaptans, chlorinated hydrocarbons are present, pump G is actuated to discharge an appropriate liquid oxidizing agent into zone A. An aqueous solution of potassium permanganate has been found satisfactory for this purpose, as it not only eliminates undesirable odors but for reasons not understood reacts with long chain toxic hydrocarbons not volatile at the temperature of the steam being used to transform a substantial portion thereof to shorter chain hydrocarbons that are volatile and flow upwardly as toxic vapors into confined space 251. [col.11, lines 42-58].

The clear implication of the above passages from Manchak Jr. '807 is that the permanganate is applied when analysis of the soil reveals the presence of hydrocarbons that are not volatile at the temperature of the fluid used for thermal stripping. The role of the permanganate injection, according to Manchak Jr. '807, is to react these hydrocarbons into

shorter chain hydrocarbons that will then be volatile at the temperature of the thermal stripping fluid. Notice particularly the implied sequence of treatment – when long chain hydrocarbon contamination is detected, no amount of thermal treatment will be effective to remove it until the permanganate treatment has reacted it to a different compound that can be thermally stripped. In other words, permanganate treatment must precede the thermal striping of this contaminant.

Notice further what Manchak Jr. '807 implies about the shorter chain hydrocarbons that the permanganate treatment supposedly creates – they are presumed to also be toxic contaminants that must be removed by thermal stripping.

Notice also what Manchak Jr. '807 implies about the quantity of permanganate that must be applied - it must be sufficient to react the total volume of contaminant to be removed, regardless of the cost of the permanganate. Further in this regard, Manchak Jr. '807 says nothing, and implies nothing, about an increase of total oxidant demand caused by the presence of natural hydrocarbons that can substantially effect the amount of permanganate required.

These are the teachings of Manchak Jr. '807. Nothing in Manchak Jr. '194 contradicts, improves or supplements these teachings.

Now compare and contrast the teachings of the Applicant's pending application to the above teachings of Manchak Jr. '807 and Manchak Jr. '194.

The Applicant's method is not directed to treating contaminants that cannot be thermally stripped without prior treatment by permanganates. To the contrary, the method is directed to thermal stripping those contaminants prior to any permanganate application. This is an exact reversal of the steps taught by Manchak Jr. '807 and Manchak Jr. '194 (permanganate before thermal stripping).

The Applicant's method is not directed to treating the total volume of the target contaminant by permanganate application. To the contrary, the method is directed to thermal stripping those contaminants to reduce the contaminant level and total oxidant demand, thus reducing the amount of permanganate required.

The Applicant's method does not presume that the reaction product of the permanganate and contaminant will include toxic contaminants that must be removed. The Applicant's method contemplates that permanganate oxidation reaction precipitates primarily manganese dioxide, which can remain in the soil. The Applicant's fist stage treatment by thermal stripping reduces the amount of permanganate required, and thus the amount of manganese dioxide produced.

These are the teachings of the Applicant's pending application. They are not taught or suggested by Manchak Jr. '807 or Manchak Jr. '194. Therefore, claims 3-5 are patentable over the combination. Claim 6 depends from claim 3 and is therefore also patentable for the reasons discussed above.

Claim 7 and its dependent claims 8, 10 and 11 have been rejected over Manchak Jr. '807 and Manchak Jr. '194 in combination with Bruso. Vinegar is added to the combination in rejected claim 12. Bruso is cited for the proposition that it is known to use a trencher to comminute soil. Applicant respectfully submits that the use of a trenching tool in combination with the steps recited in claim 7 is patentable over the cited references. Specifically, claim 7 requires that hot air be injected into the soil during comminution to thermally strip off organic compounds until such thermal stripping is no longer practically effective in further reducing the contaminant concentration level. In addition, if the concentration level of the contaminant organic compound is above the target level after the first step, the claim requires that a chemical

oxidizing agent be introduced into the soil in an amount that is effective over reasonable time to reduce the contaminant concentration level to or below the target level.

For the reasons discussed above, Manchak Jr. '807 and Manchak Jr. '194 do not teach or suggest these steps. Therefore, claim 7 and its dependent claims 8, 10 - 12 are also not obvious over the cited references.

Declaration of Inga Carus under 37 C.F.R. 1.132

As demonstrated in the above discussion, the Examiner has not established a prima facie case of obviousness from the prior art references. Even if a prima facie obviousness rejection were made out by the combination of references, however, Applicant has objective evidence of non-obviousness. In support of Applicant's position that the claims of his present invention would not have been obvious to one of ordinary skill in the art at the time the invention was made, Applicant has filed herewith a declaration under 37 CFR 1.132 of Inga Carus, Vice President of Sales and Marketing for Carus Chemical Company, the world's largest manufacturer of potassium permanganate. Ms. Carus is very familiar with and promotes the use of permanganates for the remediation treatment of hazardous waste sites.

Ms. Carus describes that permanganate oxidation is an optimal technology for groundwater contamination, particularly for chlorinated organic solvents, including trichloroethylene (TCE) and perchloroethylene (PCE). Where the organic solvents are found in dense non-aqueous phase liquids (DNAPLs), however, the contaminated liquids are not susceptible of being pumped out of the ground for treatment and must be treated with permanganate by in-situ chemical oxidation (ISCO) processes.

Ms. Carus describes what have been the two primary injection methods for ISCO treatment. The first method injects the permanganate on one side of the contaminated zone while

pumping out groundwater on the other side to create a negative pressure causing the permanganate to migrate more quickly. The second method uses injection without extraction - the permanganate is allowed to migrate naturally through the contaminated zone. These predominant prior art injection methods are referred to in the present application at paragraphs 0003-0006.

Ms. Carus also describes the importance of the permanganate being able to contact the contaminant, and that achieving contact through soil migration is difficult in dense silt and clay. The mechanical churning and mixing described in the method of the present invention greatly improves the contact. The wet impermeable clay is broken into small clumps so that the permanganate can more easily migrate into contact with PCE.

As Ms Carus points out, the other and equally significant result of first stage thermal stripping significantly reduces not just the concentration of the target contaminant, but also reduces the total oxidant demand by the stripping of natural and other hydrocarbons along with the target hydrocarbon. After the first stage treatment, the site has good soil permeability, low total oxidant demand, and a low-level concentration of volatile contaminant. These are optimal conditions for permanganate oxidation.

Ms. Carus believes that the Applicant's process of the thermal stripping while breaking up the dense soil, followed by permanganate oxidation, will be a preferred treatment plan for PCE and similar contaminants in wet impermeable soil. She regards it as a significant new treatment, did not know of anyone having performed the process before Mr. Bruso, and she does not believe that it would have been obvious to her or to others involved with hazardous waste treatment to attempt the method until it was demonstrated by Mr. Bruso.